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COMPATIBILITY OF POLYACETYLENE WITH LITHIUM BATTERY MATERIALS.(U)

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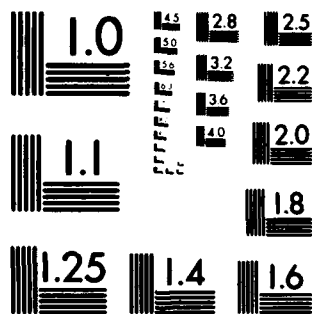
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COMPATIBILITY OF POLYACETYLENE WITH  
LITHIUM BATTERY MATERIALS

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PREPARED FOR  
THE U.S. NAVAL RESEARCH LABORATORY  
UNDER CONTRACT NUMBER  
N00014-82-C-2124

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## INTRODUCTION

↙  
The object of the research conducted under this contract is to evaluate polyacetylene ( $\text{CH}_x$ ) as a replacement for carbon as the cathode material in primary lithium/thionyl chloride ( $\text{Li/SOCl}_2$ ) and lithium/sulfur dioxide ( $\text{Li/SO}_2$ ) batteries. The choice of the  $\text{Li/SOCl}_2$  inorganic electrolyte cell is based on the fact that it is the highest energy density system known to date.<sup>1-2</sup> By itself, the favorable ratio of obtainable work to weight is not sufficient. For Navy applications, the rate at which the cell supplies energy - the power density - is very important.  $\text{CH}_x$  is a lightweight material with extremely high effective surface area (60  $\text{m}^2/\text{g}$ )<sup>3</sup> and good electrical conductivity when doped, thus making it a good candidate for an electrode in a high power density cell.

↑ *Mr. [unclear]*

This report examines the stability of  $\text{CH}_x$  in the  $\text{Li/SOCl}_2$  system and outline the approaches which are being investigated to improve the performance and stability of  $\text{CH}_x$ .

## Results

### 1. Suitability of a $\text{CH}_x$ Cathode in a $\text{Li/SOCl}_2$ Battery

Previous work has demonstrated that the electrochemistry of  $\text{CH}_x$  films involves a number of complex phenomena, including film structural reorganization,<sup>4</sup> molecular isomerization<sup>5</sup> and degradation. In addition, compatibility studies have shown that exposure of  $\text{CH}_x$  to  $\text{SOCl}_2$  causes the silvery luster of the  $\text{CH}_x$  to turn white and the normally flexible films becomes brittle, indicative of oxidative decomposition.<sup>7</sup> Although spectral, electrochemical and chemical analyses of  $\text{CH}_x$  and its breakdown products are still in progress, the prognosis for use of unmodified  $\text{CH}_x$  in a  $\text{Li/SOCl}_2$  cell is not favorable.

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## 2. Stabilization of $\text{CH}_x$ by Coating with Electroactive Polymers

The approach being taken to circumvent the problems of chemical and electrochemical degradation is to deposit an electroactive polymer coating on the  $\text{CH}_x$  substrate. The function of the coating is to provide physical protection of  $\text{CH}_x$  from the  $\text{SOCl}_2$  solution and to mediate the transfer of reducing equivalents from the  $\text{CH}_x$  to  $\text{SOCl}_2$ . Electrochemical polymerization of transition metal complex monomers has been used successfully as a means of preparing uniform, electroactive films of a wide range of redox potentials in a reproducible, controlled manner.<sup>8</sup> Polymerization can be initiated either oxidatively or reductively.

A number of polymerizable complexes of ruthenium have been synthesized, including:  $\text{Ru}(\text{trpy})(\text{bpy})(\text{vpy})^{2+}$  ( $\text{trpy}$  = 2,2',2"-terpyridine;  $\text{bpy}$  = 2,2'-bipyridine;  $\text{vpy}$  = 4-vinylpyridine),  $\text{cis-Ru}(\text{bpy})_2(\text{vpy})_2^{2+}$ ,  $\text{Ru}(\text{trpy})(\text{vpy})_3^{2+}$ ,  $\text{Ru}(\text{trpy})(\text{BPE})_3^{2+}$  ( $\text{BPE}$  = trans-1,2-bis(4-pyridyl)ethylene) and  $\text{cis-Ru}(\text{bpy})_2(\text{py}_2\text{C}_2)_2^{2+}$  ( $\text{py}_2\text{C}_2$  = bis(4-pyridyl)acetylene). All of the above complexes undergo reductively-initiated polymerization; the BPE complex can participate in an oxidative film-formation reaction as well. (Note: the use of redox polymer films-composed of the metal complexes described above- for applications in secondary (storage) batteries constitutes a separate area of research which is also being explored.)

$\text{Ru}(\text{trpy})(\text{vpy})_3^{2+}$  has been electropolymerized using  $\text{AsF}_5$ -doped  $\text{CH}_x$  as the electrode material. The resulting brown Ru-containing film was inhomogeneous and coated only a small part of the  $\text{CH}_x$  surface. The reason for the poor coating has been extensively attributed to electrochemical undoping of the  $\text{CH}_x$  (to the semiconducting state). As a result, uncompensated resistance through the  $\text{CH}_x$  film increases dramatically with consequent loss of potential control.

Further experiments along these lines are in progress to establish whether it is the complex or the nature of the reductive reaction which restricts the coating process.

The oxidative polymerization route will also be investigated using the  $\text{Ru}(\text{trpy})(\text{BPE})_3^{2+}$  complex. The potentials required to deposit the metallopolymer are sufficiently positive of the formal potential of  $\text{CH}_x^{+/0}$  that "undoping" (and loss of conductivity) should not inhibit the coating process.

Ru-modified  $\text{CH}_x$  films will continue to be examined by SEM to evaluate the uniformity of the coating; the electrochemistry and stability in non-aqueous solvents and  $\text{SOCl}_2$  will be compared to that of uncoated  $\text{CH}_x$ .

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